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TiO_2-mediated photocatalytic degradation of a textile dye derivative, bromothymol blue, in aqueous suspensions

M.M. Haque, M. Muneer*

Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

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Abstract

Photocatalysed degradation of a textile dye derivative, bromothymol blue, has been investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was monitored by measuring the change in substrate concentration as a function of irradiation time employing UV spectroscopic analysis technique. In these studies, a number of byproducts are formed during the photooxidation process, which can potentially be harmful to the environment, therefore, we have studied the mineralization of the pollutant by measuring the total organic carbon (TOC) as a function of irradiation time. The degradation kinetics were studied under different conditions such as pH, catalyst concentration, substrate concentration, different types of TiO_2 and in the presence of electron acceptors such as hydrogen peroxide (H_2O_2), potassium bromate ($KBrO_3$) and ammonium persulphate $(NH_4)_2S_2O_8$ besides molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst, titanium dioxide (TiO_2) Degussa P25, was found to be more efficient as compared with other TiO_2 powders. All the electron acceptors markedly enhanced the degradation of the pollutant under investigation.

Keywords: Photocatalysis; Bromothymol blue; Titanium dioxide; Semiconductor

1. Introduction

A wide variety of organics are introduced into the environment through various sources such as industrial effluents, agricultural runoff and chemical spills. Industrial effluents contain several non-biodegradable substrates that can be harmful to the environment [1]. One major source of these effluents is the waste arising from the industrial process, which utilizes dyes to color paper, plastic and natural and artificial fibers [2]. A substantial amount of dyestuff is lost during the dyeing process in the textile industry [2], which poses a major problem for the industry as well as a threat to the environment [2–6]. Decolourization of dye effluents has therefore acquired increasing attention. During the past two decades, photocatalytic process involving TiO_2 semiconductor particles under UV light illumination has been shown to be potentially advantageous and useful in the treatment of waste water pollutants.

There are several studies related to the use of semiconductors in the photomineralization of photo stable dyes [7–18]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature [19,20]. Briefly, when a semiconductor such as TiO_2 absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band (e^-_{cb}) leaving behind an electron vacancy or "hole" in the valence band (h^+_{vb}). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h^+_{vb} may react with surface-bound H_2O or OH^- to produce the hydroxyl radical ($OH^{\bullet}$) and e^-_{cb} is picked up by oxygen to generate superoxide radical anion ($O_2^{\bullet -}$), as indicated in Eqs. (1)–(3).

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \qquad (1)$$

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* Corresponding author. Tel.: +91 571 2703515; fax: +91 571 2702758.
E-mail address: cht12mm@amu.ac.in (M. Muneer).

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$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet -} \quad (2)$$

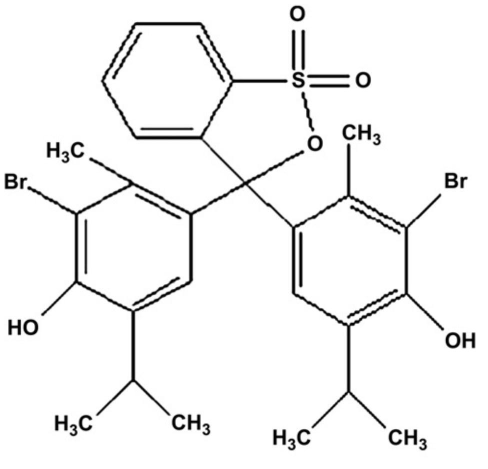
$$H_2O + h_{vb}^+ \rightarrow {}^{\bullet}OH + H^+ \quad (3)$$

It has been suggested that the hydroxyl radicals ($OH^{\bullet}$) and superoxide radical anions ($O_2^{\bullet -}$) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the dye. Alternatively, direct absorption of light by the dye, can lead to charge injection from the excited state of the dye to the conduction band of the semiconductor as summarized in the following equations:

$$Dye_{ads} + h\nu \rightarrow Dye_{ads}* \quad (4)$$

$$Dye_{ads}* + TiO_2 \rightarrow Dye_{ads}^+ + TiO_2(e^-) \quad (5)$$

Earlier studies [7–18] have shown that heterogeneous photocatalytic oxidation processes can be used for removing coloring material from dye effluent in the presence of light. The model compound bromothymol blue (BTB, **1**) is a textile dye derivative. The photocatalytic degradation of bromothymol blue using batch reactor in the presence of TiO_2 immobilized on ceramic beads and doped TiO_2 has been investigated earlier [21]. No major efforts have been made to study the detailed degradation kinetics, which is essential from the application point of view. Therefore, we have undertaken a detailed study on the photodegradation of bromothymol blue (**1**) sensitized by TiO_2 in aqueous solution examining various reaction parameters, e.g. reaction pH, substrate and catalyst concentrations, type of photocatalyst and addition of several electron acceptors.



Bromothyl blue (BTB)

$C_{27}H_{23}Br_2O_5S$

2. Experimental methods

2.1. Reagents

Analytical grade bromothymol blue was obtained from Aldrich and used as such without any further purification. Double distilled water was employed in this study to make stock solution for irradiation experiments. The photocatalyst, titanium dioxide Degussa P25, was used in most of the experiments, and other catalyst powders, namely, Hombikat UV100 (Sachtleben Chemie GmbH), PC500 (Millanium Inorganics) and TiO_2 obtained from Travancore Titanium Products (TTP), India, were used for comparative studies. Degussa P25 contains 75% anatase and 25% rutile with a specific BET surface area of 50 $m^2 g^{-1}$ and a primary particle size of 20 nm [22]. Hombikat UV100 consists of 100% pure anatase with a specific BET surface area of 250 $m^2 g^{-1}$ and a primary particle size of 5 nm [23]. The photocatalyst PC 500 has a BET surface area of 287 $m^2 g^{-1}$ with 100% anatase and primary particle size of 5–10 nm [24] and TiO_2 obtained from Travancore Titanium Products (TTP), India, has a BET surface area of 9.82 $m^2 g^{-1}$. The other chemicals such as NaOH, HNO_3, hydrogen peroxide, potassium bromate and ammonium persulphate used in the study were obtained from Merck.

2.2. Procedure

For experiments under UV light, stock solutions of the compound with desired concentration were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass was used in this study. For irradiation experiment, 250 mL of the desired solution was filled into the reactor and the required amount of photocatalyst was added and the solution was stirred for at least 15 min in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The pH of the reaction mixture was adjusted by adding dilute aqueous solution of NaOH or HNO_3. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp. IR radiation and short wavelength UV radiation were eliminated by a water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation for analysis.

2.3. Analysis

The degradation was monitored by measuring the absorbance on a Shimadzu UV–vis spectrophotometer (Model 1601), whereas the mineralization of the dye was monitored by measuring the total organic carbon (TOC) content with a Shimadzu TOC 5000A analyzer by directly injecting the aqueous solution. The absorbance of the model compound was followed at 420 nm wavelength.

3. Results and discussion

3.1. Photocatalysis of TiO_2 suspensions containing bromothymol blue

Irradiation of an aqueous solution of the BTB (**1**, 0.25 mM, 250 mL) in the presence of TiO_2 (Degussa P25, 1 $g L^{-1}$) by the "Pyrex" filtered output of 125 W medium pressure mercury lamp, lead to a decrease in the absorption intensity as well as depletion in TOC content. Fig. 1 shows the change in absorption intensity and depletion in TOC content as a function of irradiation time for the photocatalytic degradation of BTB in the absence and presence of the photocatalyst. Both the decomposition and mineralization curves can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. For each experiment, the rate constant was calculated from the plot of natural logarithm of TOC and dye concentration as a function of irradiation time. The degradation rate for the mineralization (depletion of TOC content vs irradiation time) and decomposition (decrease in absorption intensity vs irradiation time) was calculated using the formula given below:

$$-\mathrm{d}[\mathrm{TOC}]/\mathrm{d}t = kc^n$$

$$-\mathrm{d}[A]/\mathrm{d}t = kc^n$$

where TOC is the total organic carbon, A, the absorbance, k, the rate constant, c, the concentration of the pollutant, and n, the order of reaction.

Control experiments were carried out in all cases, employing unirradiated blank solutions. No observable loss of the compound occurs when the irradiation was carried out in the absence of TiO_2. The zero irradiation time readings were obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

3.2. Comparison of different photocatalysts

Titanium dioxide is known to be the semiconductor with the highest photocatalytic activity, is non-toxic, relatively inexpensive and stable in aqueous solution. Several reviews have been written, regarding the mechanistic and kinetic details as well as the influence of experimental parameters. The degradation and mineralization of bromothymol blue was tested with four different commercially available photocatalysts, namely Degussa P25, Hombikat UV100, PC500 and TTP. Fig. 2 shows the degradation rate for the decomposition and mineralization of the compound in the presence of different photocatalysts. It has been observed that the degradation of the dye derivative **1** proceeds much more rapidly in the presence of Degussa P25 as compared to other employed photocatalyst powders. In all the following experiments, Degussa P25 was used as the photocatalyst since this material exhibited the highest overall activity for the degradation of the model compound under investigation.

The better photocatalytic activity of Degussa P25, could be attributed to the fact that P25 is composed of small nano-crystallites of rutile dispersed within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating electron–hole pairs. The electron transfer, from the rutile conduction band to electron traps in anatase phase takes place. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react [25].

3.3. pH effect

An important parameter in the photocatalytic reactions taking place on the semiconductor particulate surface is the pH of the solution, since it dictates the surface charge properties of the catalyst and therefore the adsorption behavior of the pollutants. Influence of pH on the degradation of BTB (**1**) in aqueous suspensions of TiO_2 was studied at the pH range between 2 and 9 under UV light source. Fig. 3 shows the degradation rate for decomposition and mineralization of bromothymol blue as a function of reaction pH. The efficiency of degradation was found to be more or less similar in the pH

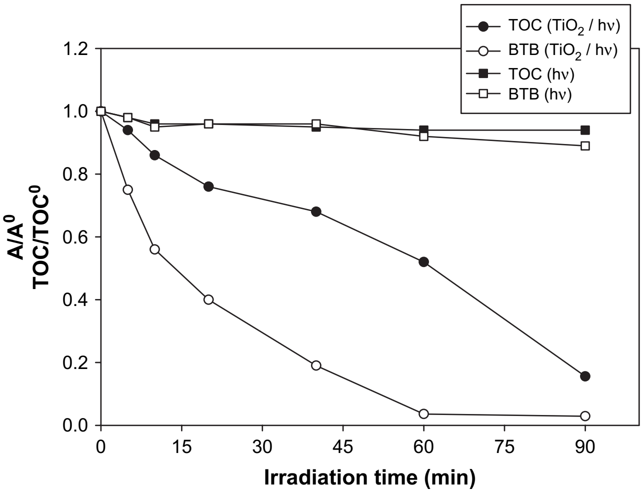


Fig. 1. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of bromothymol blue (BTB, **1**) in the presence and absence of the photocatalyst. Experimental conditions: 0.25 mM BTB, $V = 250$ mL, photocatalyst TiO_2 (Degussa P25, 1 g L^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 420 nm, cont. O_2 purging and stirring, and irradiation time = 90 min.

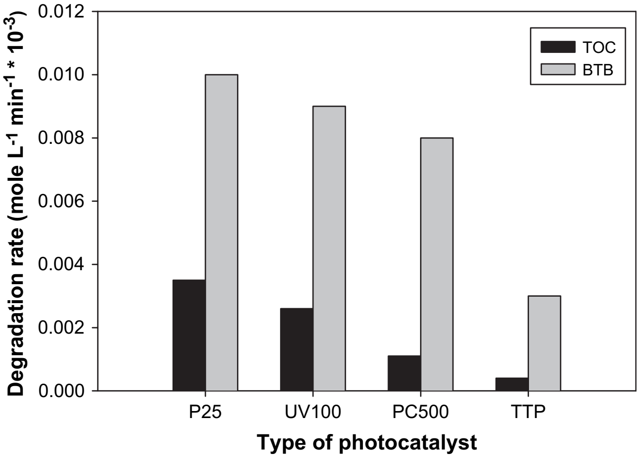


Fig. 2. Comparison of degradation rate for the mineralization (TOC depletion vs irradiation time) and for the decomposition (change in absorption intensity vs irradiation time) of bromothymol blue (BTB, **1**) in the presence of different photocatalysts. Experimental conditions: 0.25 mM BTB, $V = 250$ mL, photocatalysts: TiO_2 (Degussa P25 1 g L^{-1}), Sachtleben Hombikat UV100 (1 g L^{-1}), PC500 (1 g L^{-1}), TTP (1 g L^{-1}), and irradiation time = 90 min.

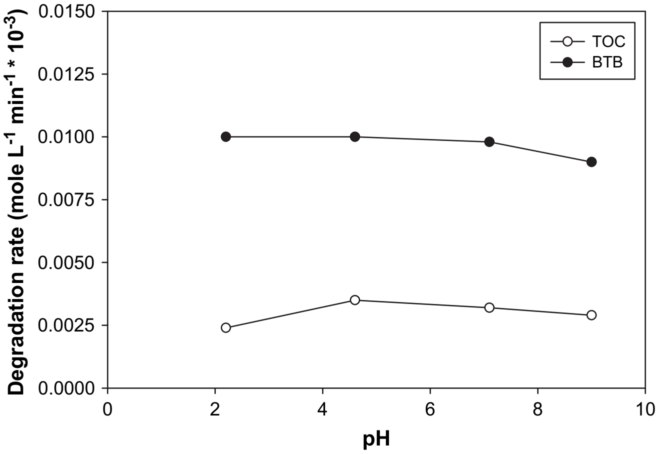


Fig. 3. Influence of pH on the degradation rate for the mineralization and decomposition of bromothymol blue (BTB, **1**). Experimental conditions: 0.25 mM BTB, $V = 250$ mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), reaction pH (2.2, 4.6, 7.1 and 9.0), and irradiation time = 90 min.

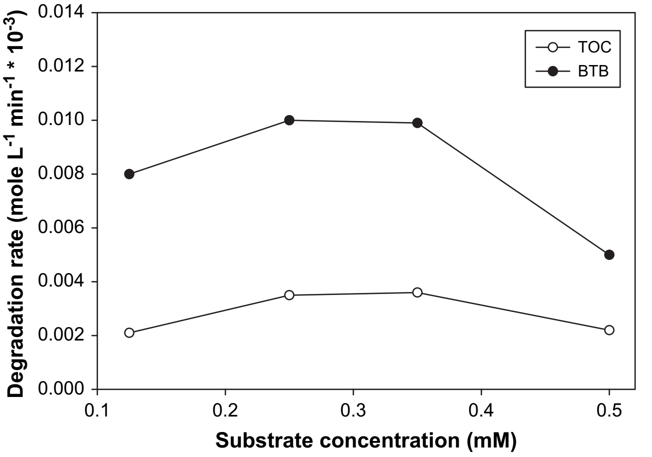


Fig. 5. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of bromothymol blue (BTB, **1**). Experimental conditions: BTB concentration (0.15, 0.25, 0.35 and 0.5 mM), $V = 250$ mL, photocatalyst TiO_2 (Degussa P25, 1 g L^{-1}), and irradiation time = 90 min.

range studied within the experimental error limits, except that slight lower mineralization rates were observed when the reaction was carried out at pH 2.2.

It has been found that when the reaction of the dye derivative 1 was carried out at pH 9.0, there was appearance of new absorption peak at 645 nm besides its λ_{max} of 420 nm as shown in Fig. 4. The absorption intensities of the peaks that appeared at these wavelengths were found to decrease as a function of irradiation time. We have followed the decrease in absorption intensity at 420 nm for determining the degradation rate.

3.4. Effect of substrate concentration

It is important both from mechanistic and application points of view to study the dependence of photocatalytic reaction rate on the substrate concentration. Hence, the influence of substrate concentration on the degradation rate was studied at different concentrations varying from 0.15 to 0.5 mM. Fig. 5 shows the degradation rate for the decomposition and mineralization of the dye as a function of substrate concentration employing Degussa P25 as photocatalyst (1 g L^{-1}). It was observed that the degradation rate was found to increase with the increase in substrate concentration from 0.12 mM to 0.35 mM. A further increase in substrate concentration leads to decrease in the degradation rate of the dye. This may be due to the fact that as the initial concentrations of the dye increase, the color of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. Hence, the generation of relative amounts of OH and $O_2^{\bullet-}$ on the surface of the catalyst does not increase, as the intensity of light and the irradiation time are constant. Conversely, their concentrations will decrease with increase in concentration of the dye as the light photons are largely absorbed and prevented from reaching the catalyst surface by the dye molecules. Consequently, the degradation efficiency of the dye decreases as the dye concentration increases.

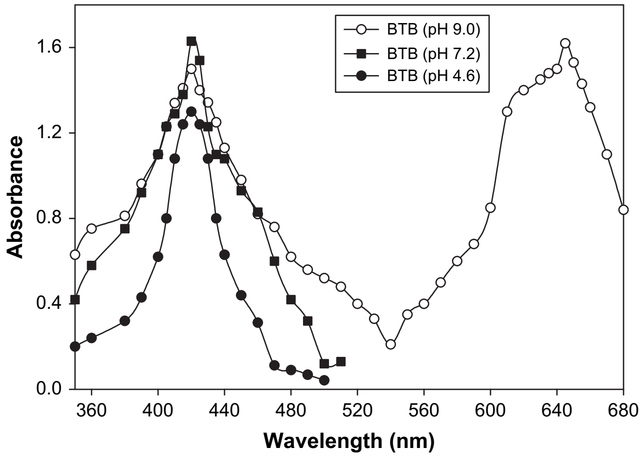


Fig. 4. Absorption spectra of the dye derivative bromothymol blue (BTB, **1**) at pH values 4.6, 7.1 and 9.0, showing the appearance of a new peak at wavelength 645 nm at pH 9.0.

3.5. Effect of catalyst concentration

The influence of the photocatalyst concentration on the degradation kinetics of bromothymol blue was investigated using different concentrations of Degussa P25 varying from 0.5 to 3 g L^{-1}. Fig. 6 shows the degradation rate for the decomposition and mineralization of the pollutant as a function of catalyst concentration. It could be seen from the figure that the addition of photocatalyst improves the degradation rate of the pollutant under investigation, which is the characteristic of heterogeneous photocatalysis and results are in agreement with a number of studies reported earlier [26–28].

The adsorption of the dye derivatives on the surface of the photocatalyst was investigated by stirring the aqueous solution in the dark for 24 h in a round-bottomed flask containing varying amounts, 0, 0.5, 1, 2 and 3 g L^{-1}, of photocatalyst.

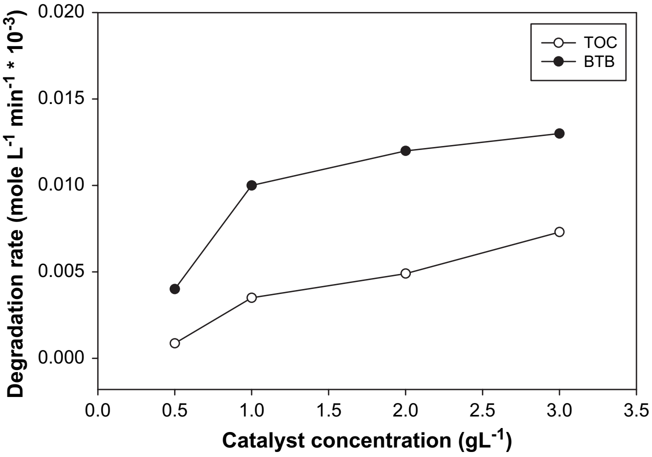


Fig. 6. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of bromothymol blue (BTB, **1**). Experimental conditions: 0.25 mM BTB, $V = 250$ mL, photocatalyst: TiO_2 (Degussa P25 0.5, 1, 2 and 3 g L^{-1}), and irradiation time = 90 min.

Analysis of the samples after centrifugation indicates no observable loss of the dye.

3.6. *Effect of electron acceptors*

Since hydroxyl radical appears to play an important role in the photocatalysis, electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate were added into the solution in order to enhance the formation of hydroxyl radicals and also to inhibit the (e^-/h^+) pair recombination. The degradation rate for the decomposition of bromothymol blue in the presence of various electron acceptors is shown in Fig. 7. All the additives showed a beneficial effect on the degradation of the model compound.

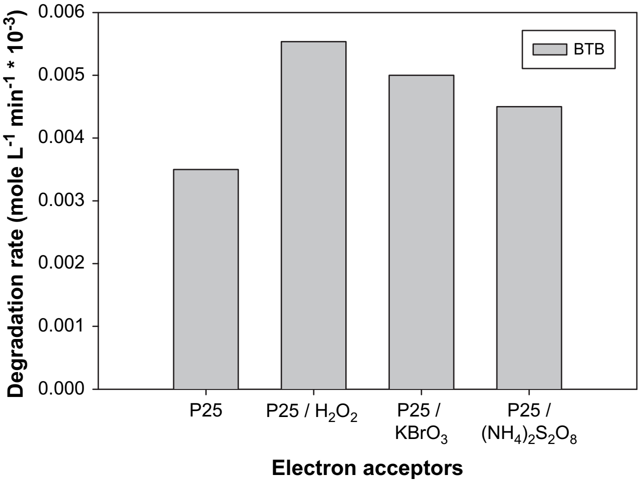


Fig. 7. Comparison of degradation rate for the decomposition of bromothymol blue (BTB, **1**) in the presence of different electron acceptors. Experimental conditions: 0.25 mM BTB, $V = 250$ mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptor: H_2O_2 (10 mM), $KBrO_3$ (3 mM) and $(NH_4)_2S_2O_8$ (3 mM), and irradiation time = 90 min.

4. Conclusion

TiO_2 can efficiently catalyze the photodegradation of the dye derivative bromothymol blue in the presence of light and oxygen. The results of this study clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rates of the model compound, which is essential for any practical application of photocatalytic oxidation processes. Degussa P25 was found to be a more efficient catalyst as compared to other TiO_2 powders. The electron acceptors have been found to enhance the degradation rate of the pollutant.

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